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Microstructural and Electrical Characterization of Barium Strontium Titanate-based Solid Solution Thin Films Deposited on Ceramic Substrates by Pulsed Laser Deposition

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ABSTRACT

Ferroelectrics are multicomponent materials with a wealth of interesting and useful properties, such as piezoelectricity. The dielectric constant of the BSTO ferroelectrics can be changed by applying an electric field. Variable dielectric constant results in a change in phase velocity in the device allowing it to be tuned in real time for a particular application. The microstructure of the film influences the electronic properties which in turn influences the performance of the film. $Ba_{0.6}Sr_{0.4}Ti_{1-y}(A^{3+}, B^{5+})_yO_3$ thin films, of nominal thickness of 0.65 μm, were synthesized initially at substrate temperatures of 400°C, and subsequently annealed to 750°C, on $LaAlO_3$ (100) substrates, previously coated with LaSrCoO conductive buffer layer, using the pulsed laser deposition technique. The microstructural and physical characteristics of the post-annealed thin films have been studied using x-ray diffraction, scanning electron microscopy, and nano indentation and are reported. Results of capacitance measurements are used to obtain dielectric constant and tunability in the paraelectric ($T>T_c$) regime.

INTRODUCTION

Ferroelectrics are multicomponent materials with a wealth of interesting and useful properties, such as piezoelectricity and paraelectricity. These properties derive from their non-centrosymmetric crystal-lattice structure in which spontaneous polarization is observed. The most widespread and potentially important use for ferroelectrics exists in the area of nonvolatile random access memories (NVRAM). Ferroelectrics are also of interest in the paraelectric regime for voltage-tunable, radio frequency, and microwave phase shifters, filters, and true-time delay devices for electronic scanning antenna technology [1]. The critical materials parameters for many microwave device designs are: low dielectric constant, high tunability, low-temperature Curie peak (T_c), low dielectric loss tangent, low leakage current and small temperature coefficient of permittivity.

For electrically tunable microwave devices with a coplanar waveguide structure, BST is used as an active dielectric layer in thin-film form [2]. To achieve a high dielectric constant and a low dielectric loss tangent (tan δ), the BST film is usually grown epitaxially on single-crystal substrates such as $LaAlO_3$ (LAO) [a=0.3793 nm, α=1ppm/°C], which has a comparatively small dielectric constant (≈25) and a low dielectric loss (loss tangent $<10^{-4}$), both necessary for microwave applications [3]. For phase shifting ceramics, it is desirable to operate the device in the paraelectric region,

hence the desire for low T_c [4]. However, in general, the higher the dielectric constant, the more tunable the ceramic will be [4]. By adding 40 mol% $SrTiO_3$ to $BaTiO_3$, the Curie peak can be shifted from 120 to –5°C but a relatively high dielectric constant can be maintained above T_c. For capacitor ceramics of perovskite structure, doping in small amounts with acceptor ions on Ti sites can greatly affect dielectric properties [4, 5]. Acceptor dopants are defined as ions with a lower valency than the ions they replace, while donor dopants are ions with higher valency. Chan et al. [5] postulated that acceptor impurities are mostly compensated for by oxygen vacancies.

We have investigated and report the microstructural and electrical characterization of selected barium strontium titanate-based solid solution thin films deposited on $LaAlO_3$ ceramic substrates by pulsed laser deposition.

EXPERIMENTAL

Selected charge-balanced binary substitutions, using $A^{3+} = Y^{3+}$and Sc^{3+} and $A^{5+} = Ta^{5+}$ were made for Ti^{+4} to obtain $Ba_{0.60}.Sr_{0.40}Sc_{0.05}Ta_{0.05}Ti0_{.90}O_3$ and $Ba_{0.60}.Sr_{0.40}Y_{0.05}Ta_{0.05}Ti0_{.90}O_3$ targets. Starting materials of 99.9%$ purity or better precursors were mixed until homogeneous, then compacted with steel die and calcined in air at 1100°C for 8h. The calcined materials were then reground to powders with 75 μm or smaller grain size, pressed at 350 MPa (50 kpsi) in an isostatic press, and sintered at 1450-1550°C for 40 h in air. Details can be found in reference [1].

The experimental apparatus consists of a pulsed laser deposition chamber equipped for optical diagnostics. The 248-nm output of an excimer laser (Lambda Physik, EMG 300 MSC) was directed through a 50-cm focal length lens and focused at 45° near the target, which was mounted inside a stainless-steel chamber on a high-vacuum, rotating holder. The details of this deposition technique are given elsewhere [6]. In this work thin films of $Ba_{0.60}.Sr_{0.40}Sc_{0.05}Ta_{0.05}Ti_{0.90}O_3$ (DP1) and $Ba_{0.60}.Sr_{0.40}Y_{0.05}Ta_{0.05}Ti_{0.90}O_3$ (DP2), were deposited by the PLD technique on 1 to 2 cm^2 LAO (100) substrates, previously coated with LaSrCoO (LSC) conductive buffer layer, deposited also by the PLD technique. Both, the BST film and the LSC buffer layers, were deposited at about 400°C, using 550 mJ laser energy, at 10 Hz repetition rate, and 26.6×10^{-4} Pa partial oxygen pressure [1 mTorr = 1.33×10^{-4} Pa], for 45 minutes. Prior to film synthesis the substrates were cleaned for 5 minutes in warm (70-75 °C) methanol and ethanol baths and rinsed in warm (70-75 °C) distilled water for another 5 minutes. All films were subsequently annealed at 750°C for 45 minutes in a tube furnace in a continuous oxygen flow.

The microstructure of the films was observed by optical and scanning electron microscopy (SEM); the crystallinity of the films was determined by Glancing Angle X-ray Diffraction (GAXRD); the thickness of the films was determined with the aid of a Tencor profilometer; and the modulus of elasticity (Young's Modulus) and the hardness of the films were determined with the aid of a nanoindenter, using a Berkovich pyramid diamond indenter.

Cylindrical electrodes of various sizes were placed on the DP1(DP2)/LSC/LAO structure. Unfortunately, each electrical pad was shorted to the LSC ground plane such that electrical measurements could not be made using these contact pads as intended. Instead an HP 16034E test fixture was used for electrically characterize of the samples.

The capacitance of the test fixture was measured before sample insertion. Each sample was loaded into the test fixture using the spring loading of the test fixture; with the electrical pin on the low bias side contacting the back of the 20 mil thick substrate and the electrical pin on the high bias side contacting the surface of the film. An alligator clip attached from the low bias side was clipped to one of the contact pads thus making electrical contact to the ground plane of the capacitor structure. A universal LCR meter (120 Hz and 1kHz) was used in conjunction with the test fixture to measure the capacitance and resistance of the sample. If sufficient contact pressure was made using the bias pins, consistent results were obtained. If too much pressure is applied the pin breaks through the thin film and makes electrical contact to the LSC ground plane. If not enough pressure is applied inconsistent results are obtained.

RESULTS AND DISCUSSION

Thickness and Adhesion

The average thickness of the composite structure, DP1 (DP2) and LSC films, was 1.3 μm. Since the synthesis of the DP1 (DP2) film and LSC film took place under identical deposition parameters, we assumed that the average thickness of each film was 0.65 μm. These thicknesses are smaller than those predicted using the laser ablation energy.

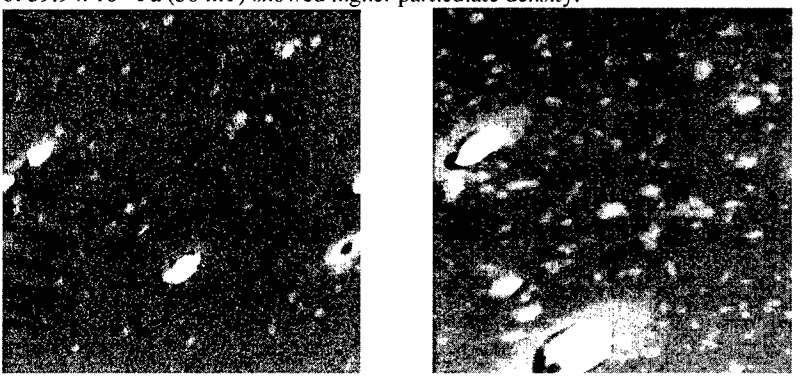
The adhesion of the BST and the LSC film and the LSC on the LAO substrate was excellent. All films passed the standard "scotch-tape pull test". Furthermore, neither of the films delaminated during the measurement of the hardness by the nano indenter and during the setup of the electrical measurements.

We also observed that the adhesion of the structure, DP1 (DP2) film and LSC film, deposited at ambient temperature, followed by subsequent annealing at 750°C was poor, resulting in film delamination even with slight finger pressure. However, the adhesion was improved dramatically when the synthesis of the films took place at higher substrate temperatures. This may be attributed to the increased thermal diffusion and consequent alloying of the films on the underlying substrate due to the increased deposition temperature.

Microstructure

The microstructure and morphology of the BST films was determined using optical microscopy and SEM. All films observed by naked eye and metallographic microscopy exhibited red and green elliptical striations, indicative of the thickness variation throughout the substrate, an inherent disadvantage of the PLD technique. After annealing, the color of the DP1 films became white opaque, which is indicative of the existence of the perovskite phase [7]. The surface of the films, before and after annealing, was relatively very smooth on a macroscopic and microscopic scale, as observed in the metallographic and scanning electron microscopes. Due to that surface smoothness, it was very difficult to obtain better quality SEM photomicrographs. However, particulates, expelled parts of the PLD target, were evident on the surface of

the films (Fig. 1a and 1b). Initial depositions of films at higher oxygen partial pressure of 39.9 x 10^{-4} Pa (30 mT) showed higher particulate density.



(a) (b)

Fig. 1 Scanning Electron Photomicrographs: (a) DP1 (2,000 X), (b) DP 2 (2,000 X)

Glancing Angle X-ray Diffraction

The GAXRD analysis showed that, while all pre-annealed films were amorphous, all post-annealed films were crystalline. The unit cell of all annealed films belonged to the cubic system. The average lattice constant "*a*" is about 0.398 nm, in very good agreement with other published values [8]. The diffraction pattern of all post-annealed films exhibited all the peaks from the diffraction pattern of the target. Some extra peaks observed in the film pattern were identified and are attributed to the underlying LAO substrate.

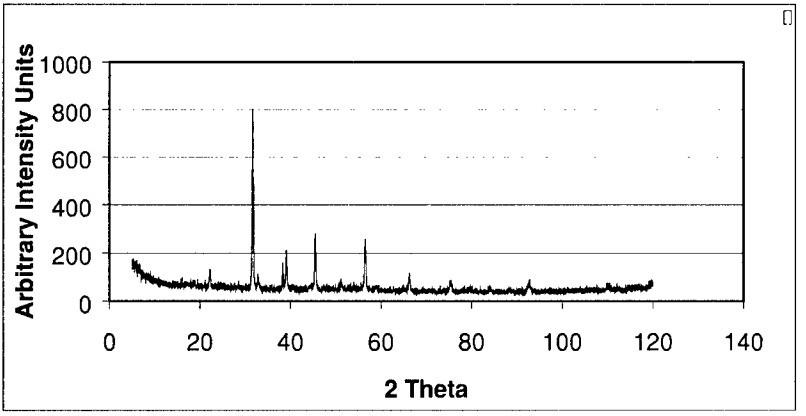


Fig. 2. Typical XRD pattern of post-annealed DP1 film.

Nanohardness and Modulus of Elasticity

The nanohardness and modulus of elasticity profile of all films determined up to 2000 nm indentation depth, at 200 nm intervals, is shown in Table 1. In order to minimize the substrate effect on the film measurements, it is recommended that, the depth of indentation must be between 10% and 25% of the total film thickness [9]. To minimize the statistical error and the effect of the indentation plastic zone on the values of the measured film properties, all measurements were averaged over nine indentations for every indentation depth, each indentation being 50 μm apart from each other. Therefore, the modulus of elasticity and the hardness of the DP1 and DP2 films, defined at 200 nm (Table 1) were 118 ± 5.30 and 103 ± 0.40 GPa, and 4.22 ± 0.44 and 3.58 ± 0.95 GPa, respectively. As it can be seen in Table 1, the barium strontium titanate films containing Scandium are slightly harder than the BST films containing Yttrium. The hardness and modulus of elasticity of the LSC film can be deduced from the corresponding values at 800 nm (Table 1).

Depth (nm)	Modulus of Elasticity (GPa)		Hardness (GPa)	
	DP1	DP2	DP1	DP2
200	118 ± 5.30	103 ± 0.40	4.22 ± 0.44	3.58 ± 0.95
400	146 ± 21.4	130 ± 19.30	5.03 ± 1.09	5.00 ± 1.13
600	153 ± 10.91	165 ± 9.61	5.39 ± 0.55	5.83 ± 0.22
800	187 ± 4.33	181 ± 7.64	5.67 ± 0.19	5.23 ± 0.32
1200	177 ± 8.65	186 ± 44.90	6.04 ± 0.29	5.24 ± 1.71
2000	190 ± 31.4	215 ± 7.30	4.31 ± 1.48	6.46 ± 0.610

Table 1. Modulus of elasticity and hardness of post-annealed films

Dielectric Properties

The measured resistance of the film was greater than 10 MΩ. The area of the pin is estimated to be 1x 10^{-7} m^2 thus yielding a resistivity, at room temperature, of about 10^9 Ω-cm for films estimated to be 6500 Å thick. The $Ba_{0.60}.Sr_{0.40}Sc_{0.05}Ta_{0.05}Ti_{0.90}O_3$ sample was measured at room temperature to have a capacitance between 6.0-6.6 pF and dissipation factor between 0.006-0.019, and 7.4-7.7 pF and 0.011-0.025 over the surface of the sample at 120Hz and 1 kHz, respectively, and capacitance of 5.8-6.8 at 1 MHz. The capacitance of the $Ba_{0.60}.Sr_{0.40}Y_{0.05}Ta_{0.05}Ti_{0.90}O_3$ sample was measured at room temperature to have a capacitance between 7.1-8.0 pF and dissipation factor between 0.014-0.017, 6.6-7.6 pF and 0.017-0.094 over the surface of the sample at 120Hz and 1 kHz, respectively, and capacitance of 7.6-8.0 at 1 MHz . At 1 MHz, the capacitance of each sample was measured as a function of temperature and applied voltage. The capacitance for the $Ba_{0.60}.Sr_{0.40}Sc_{0.05}Ta_{0.05}Ti_{0.90}O_3$ sample changed by less than 15% over the temperature range from –70 to 20°C and the tunability was less than 10% at 60 V/μm. At 1 MHz, the capacitance of the sample was measured as a function of temperature and applied voltage. The capacitance for the $Ba_{0.60}.Sr_{0.40}Y_{0.05}Ta_{0.05}Ti_{0.90}O_3$ sample changed

about 60% over the temperature range from –70 to 20°C with peak in capacitance at about –20°C and the tunability was less than 15% at 60 V/μm. Breakdown field strengths were about 80 kV/cm for these samples.

CONCLUSIONS

The crystallinity, surface morphology, adhesion, modulus of elasticity, hardness and dielectric constants of selected $Ba_{0.6}Sr_{0.4}Ti_{1-y}(A^{3+}, B^{5+})_yO_3$ thin films synthesized on LAO (100) substrates, previously coated with LSC conductive buffer layer, using the pulsed laser deposition technique. As shown by GAXRD analysis, all post-annealed films were crystalline. The capacitance for the $Ba_{0.60}.Sr_{0.40}Sc_{0.05}Ta_{0.05}Ti_{0.90}O_3$ sample changed by less than 15% over the temperature range from –70 to 20°C and the tunability was less than 10% at 60 V/μm. The capacitance for the $Ba_{0.60}.Sr_{0.40}Y_{0.05}Ta_{0.05}Ti_{0.90}O_3$ sample changed about 60% over the temperature range from –70 to 20°C with peak in capacitance at about –20°C and the tunability was less than 15% at 60 V/μm. Breakdown field strengths were about 80 kV/cm for these samples.

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